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and into pyromucic acids under the same conditions as chondrosic acid, hence it was concluded that the two acids were similar in their structure, namely, that in both an oxygen bridge existed between the  $\alpha$ - and  $\alpha_1$ -carbon atoms.<sup>4</sup>

6. The anhydrodicarboxylic acids (derived from hexoseamines) have as many asymmetric carbon atoms in their molecule as the corresponding acids derived from hexoses. Therefore, there are possible only two optically inactive anhydrodicarboxylic acids: namely, one corresponding to mucic and the other to allomucic acid. This consideration limits the possibilities of configuration of epichondrosic acid to anhydromucic, or anhydroallomucic. The fact that chondrosamine forms a phenyl osazone identical in its properties with that of allose decides the choice between the two configurations in favor of anhydroallomucic.

7. Regarding the configuration of chondrosine the choice remains between that of *l*-allosamine or of *l*-altrosamine. Both anhydroallomucic and anhydrotalomucic acids are obtainable from chondrosamine depending on the procedure in preparation.

It was attempted to prepare chondrosaminic acid synthetically from ribosimine by the action of prussic acid. The acid obtained in this manner had the composition of hexosaminic acid, C = 37.02%, H = 6.58%, and N = 7.44% (theory, C = 36.92, H = 6.66, N = 7.18). M. P. = 198°C.,  $[\alpha]_D^{28} = -9.4^\circ$ . The acid was evidently epimeric with chondrosaminic, and on treatment with nitric acid it should have yielded chondrosic acid. Unfortunately for lack of material this experiment had to be deferred.

<sup>1</sup> Fischer, E., and Leuchs, H., *Berlin, Ber. D. chem. Ges.*, **36**, 24 (1903).

<sup>2</sup> Irvine, J. C., and Hynd, A., *London, J. Chem. Soc.*, **101**, 1128 (1912); **105**, 698 (1914).

<sup>3</sup> Levene, P. A., and La Forge, F. B., *J. Biol. Chem.*, **18**, 123 (1914).

<sup>4</sup> Fischer, E., and Tiemann, F., *Berlin, Ber. D. chem. Ges.*, **24**, 2139 (1891).

## THE FREEZING-POINT-SOLUBILITY LAW FOR IDEAL SOLUTIONS

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When a solution is formed by mixing together two completely miscible pure liquids, it is found that when the two constituents resemble each other very closely the formation of the solution takes place without appreciable heat-effect or volume-change. Such solutions have been termed *ideal solutions*; and experiments have shown that the vapor pres-

sure  $p_A$  of any constituent A in such a solution is proportional to the mole-fraction  $x_A$  of that constituent in the solution. This law is expressed in differential form by the equation:  $dp_A = k dx_A$ .

From this relation, with the aid of thermodynamics, we may derive the other laws of ideal solutions. Most of the experimental data at present available for illustrating the application of these laws to specific cases have been derived from direct measurements of the vapor-pres-  
sures themselves. It seemed therefore desirable to secure some additional experimental data which would serve as examples illustrating the character of the results given by some of the other laws.

The freezing-point-solubility law was chosen as the first one to be studied in this connection because it happens that this law offers a convenient as well as exact method for testing the accuracy with which a given solution obeys the laws of ideal solutions.

For an ideal solution of two substances, A and B, it can be shown thermodynamically that the following equations express the change of freezing-point caused by an increase in the mole-fraction of each component:

$$\frac{dT}{dx_A} = \frac{RT^2}{L_A x_A}, \quad \frac{dT}{dx_B} = \frac{RT^2}{L_B x_B}$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $L$  the heat of fusion per mole, and  $x$  the mole-fraction, in solution, of the substance indicated by the subscript. At the eutectic point it is evident that these two equations must hold simultaneously; and by eliminating  $x_A$  and  $x_B$  from them we can calculate the eutectic temperature for the system under consideration. The purpose of this investigation was to test in this way the validity of these equations for the three two-com-  
ponent solutions which can be formed from the three substances benzene, diphenyl, and naphthalene. For this purpose it is necessary to know the heat of fusion and melting-point of each substance.

Satisfactory values of the molar heats of fusion of benzene and naphthalene were available; that of benzene had been determined by Demerliac and by J. Meyer to be 2370 calories, and that of naphthalene by Alluard and by Pickering as 4560 calories. It was, however, necessary to determine that of diphenyl. For this purpose, weighed amounts (about 30 grams) of diphenyl in stoppered test-tubes were transferred from a mercury bath at  $71^\circ$  to a calorimeter, consisting of a silvered vacuum-tube filled with water; and the rise in temperature (about  $3^\circ$ ) was measured with a Beckmann thermometer. The calorimeter was then cooled to its original temperature by dropping in a weighed piece of dry

ice taken from an air bath at  $-2^{\circ}$  where it was suspended on a silk thread. As an additional check on the water-equivalent of the calorimeter the first operation was then repeated, using however test-tubes containing naphthalene instead of diphenyl. The heats of fusion of ice and of naphthalene being known, that of diphenyl could be readily calculated from these experiments. It was thus found to be 4020 calories per mole.

The freezing-points of the pure substances and the eutectic points of the three solutions were determined by the equilibrium method. The apparatus consisted of a Baudin thermometer standardized by the National Bureau of Standards and a small silvered cylindrical vacuum-tube which was heated (or cooled) to the required temperature previous to beginning the experiment. For temperatures higher than that of the room, the crystals (pure substance or eutectic mixture) were melted in a small casserole, and the liquid (about 25 cc.) was poured into the vacuum-tube and the thermometer inserted. When the temperature of crystallization had been reached more of the crystals were added, after which the thermometer reading soon became constant and remained so (within less than  $0.1^{\circ}$ ) for ten or fifteen minutes, with constant stirring and tapping of the thermometer. For temperatures lower than room-temperature the solid crystals (previously cooled, in the case of the eutectic mixture) were placed in the vacuum-tube, and equilibrium between the crystals and liquid in contact with the thermometer bulb was obtained as before. In this way the three melting-points and the three eutectic temperatures could be easily measured with an accuracy of at least  $0.1^{\circ}$ . The constancy of the three melting-points within this limit is sufficient criterion of the purity of the materials employed.

In order to calculate the eutectic temperatures from the freezing-point equations given above, these equations were first integrated on the assumption that  $L$  is independent of  $T$  for the ranges involved. This assumption is justified in the case of benzene and naphthalene by the small differences between the specific heats in the solid and liquid states. In the case of diphenyl specific-heat data are not available, but the assumption seemed justifiable by analogy. The two integrals are:

$$2.303 \log_{10} x_A = - \frac{L_A (T_{0A} - T)}{RT_{0A}T}; \quad 2.303 \log_{10} x_B = - \frac{L_B (T_{0B} - T)}{RT_{0B}T};$$

where  $T_{0A}$  and  $T_{0B}$  are the absolute melting-points of the pure substances. By solving these two equations simultaneously (with the aid of the axiom,  $x_A + x_B = 1$ ) values of the eutectic temperature  $T$  were obtained.

The melting-points of the pure substances were found to be: Benzene,

$C_6H_6$ : 5.48°. Diphenyl,  $C_6H_5C_6H_5$ : 68.95°. Naphthalene,  $C_{10}H_8$ : 80.09°. The directly measured values and the computed values of the three eutectic temperatures were found to be as follows:

Benzene-naphthalene; measured: -3.48°; computed: -3.56°.

Benzene-diphenyl; measured: -5.8°; computed: -6.1°.

Naphthalene-diphenyl; measured: 39.4°; computed: 39.4°.

The close agreement between the calculated and observed values of the eutectic temperatures shows that these three solutions are very close to ideal solutions in their behavior; for this method of testing them is a very rigorous one.

The above given differential equations represent the most generally applicable freezing-point and solubility law which we have at present. By means of this law we can calculate the freezing-point of a given solution or the solubility of a given solid in a liquid for all solutions which fulfil the necessary conditions. These conditions are (1) the heat of dilution of the solution for the range of concentration involved must be practically zero; and (2) the dilution of the solution must not be accompanied by the occurrence of a chemical reaction of any kind. The quantity  $L$  in the equations represents in general the molal heat of solution of the crystalline substance in its own saturated solution. For ideal solutions this heat of solution is of course identical with the heat of fusion. The above law should be generally employed in place of the more common 'dilute solution' laws, which are only special cases of it.

In closing this paper it may be worth while to point out two examples of the use of the equation given above which do not seem to be familiar to most chemists, and especially to those chemists in whose special fields of work they are of chief interest.

1. The results of the search for some general principle concerning the solubility of substances in each other is usually summed up by restating the old principle that *similia similibus solvuntur*. In the light of our present knowledge we can, however, go somewhat further than this simple qualitative statement, and can formulate the following quantitative principle:

When a crystalline substance A is dissolved in any solvent B with which it forms an ideal solution, its solubility (expressed in terms of its mole-fraction in the saturated solution) is *entirely independent of the nature of the solvent B*, and is therefore the same in all such solvents. The solubility depends merely upon the temperature and upon the melting-point and heat of fusion of the crystals A, from which data it can in fact be readily calculated. This important principle, which follows directly from the above equations does not seem to have been gener-

ally appreciated, although it was discovered in 1893 by Schröder (*Zs. physik. Chem.*, **11**, 449).

2. Another important use to which the general freezing-point-solubility law could be put would be in settling the frequently discussed question as to whether racemates exist as such in the liquid state, and if so, to what extent. This question could be most certainly and definitely decided for any given pair of optical isomers simply by determining the freezing-point diagram for the system and applying the general law. The exact amount of racemate present in the liquid state and the manner in which it varies with the temperature could also be computed; for a solution composed of two optical isomers forms one of the most perfect examples known of an ideal solution, and the laws of such solutions would apply with great exactness over the whole range of concentrations. In addition to the freezing-point diagram, the latent heats of fusion and the heat of dilution would also be needed in order to work out the problem completely. The main point which it is desired to emphasize here is simply that the ideal solution laws are capable of giving a complete and quantitative answer to such a question as this, an answer concerning the correctness of which no reasonable doubt could be felt.

## MERCURY DERIVATIVES OF AROMATIC AMINES. I. STRUCTURE OF PRIMARY AND SECONDARY *p*-AMINO-PHENYLMERCURIC COMPOUNDS

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During the year 1902, the question of the structure of the mercury derivatives of the aromatic amines was the occasion of a polemic between L. Pesci<sup>1</sup> and O. Dimroth.<sup>2</sup> The former ascribed the complex structure (I) to the mercuriated primary and secondary amines ( $R = H$  or alkyl), while Dimroth advocated the simple monomolecular formula (II), basing his views upon arguments which Pesci was unable to controvert. Subsequent workers have used the monomolecular formula

